TITLE: ASSEMBLAGE ANALYSIS - IDENTIFICATION OF CONTAMINATION SOURCES

By: E. R. Crutcher
Boeing Aerospace Company
Quality Assurance Laboratories

## ABSTRACT

It has been found that contamination samples of less than one milligram often contain a sufficient variety of particulate types to reconstruct a history of contamination exposure. This approach involves the use of analytical light microscopy, and related techniques, to identify source-characteristic assemblage of particulates. Sources are identified as belonging to one of four major categories: auto-generated, function-generated, facility-generated, or activity-generated. The first two indicate system reliability and design-operational environment compatibility. The last two involve production related problems of facility control or failure to properly isolate the part from externally generated contaminates.

Sources cannot generally be identified through the identification of a single particle species, but only through a combination of species in specific size ranges and present in "reasonable" proportions with respect to other members of the assemblage. This paper presents the basis for criteria used to identify an assemblage and the analytical support required to evaluate such a sample. Examples of common assemblages are given as well as precautions against conclusions based on too few members of an assemblage. A brief final statement is included regarding the benefits of this type of program support.

# ASSEMBLAGE ANALYSIS - IDENTIFICATION OF CONTAMINATION SOURCES

## 1.0 INTRODUCTION

Contamination problems occasionally plague programs attempting to maintain the cleanliness levels required by increasingly sophisticated instrumentation. When such problems arise it is important to identify the source, or sources, of that contamination. The discovery of a source can lead to improvements in instrument or system design, improved clean room technology, or the identification of a need for tighter specification control and training. If the source is not identified, contamination problems can require very expensive rework and training in response to an ambiguous problem.

The heterogeneity and small sample size of most contamination samples preclude most customary analytical approaches. Assemblage analysis uses sample heterogeneity as an essential source labeling device and can easily be applied to clean room problems where the total sample size is less than one microgram.

Assemblage analysis has not completely removed the ambiguity from all contamination problems, but in many instances it has resulted in the unequivocable identification of a source, thus providing a quick and relatively inexpensive specific solution.

Assemblage analysis is a term borrowed from archeology where it refers to a technique used to monitor cultural development and change through time. Here it refers to a methodology used to identify sources of contamination through the recognition of different types of particulate assemblages characteristic of specific sources. A "source" can be a point of origin, a generation mechanism, a transport mechanism, or some combination of the three. There are five basic assumptions which underlie this technique:

1. A source generates more than one type of particulate or aerosol.

2. The particulate generated by a source reflects the mechanism of production, the material being acted upon, and the environmental conditions at the time and place of generation.

3. Once generated the particulate behaves in a predictable manner, subject to gravitation, filtration, and chemical or physical alteration.

4. Specific transport mechanisms deliver particulate which has specific physical parameters that reflect the method of transport, the distance of transport, and obstacles or scrubbing devices designed to clean the mobil phase in the transport system.

5. The method used to collect the sample and the subsequent analytical methods do not significantly distort the data.

These assumptions, and the experience of the analyst, combine to form the foundation of this technique.

## 2.0 DEFINITION OF ASSEMBLAGE TYPES

There are four main assemblage types: auto-generated, function generated, facility generated, and activity generated. Each of these types is characterized by the relationship between the assemblage and the system being contaminated.

2.1 Auto-generated Contaminates: non-wear derivatives of the system's structural materials.

Some materials are incompatible with their operational environment, or behave in a manner detrimental to the mission goals in specific environments. Two examples of these types of problems are the volatile-condensibles in some materials used early in the space program[1], and the particulate generation associated with the dielectric breakdown of FEP Teflon in synchronous earth orbit[2]. Many additional, more routine examples exist, such as gasket incompatibility with some hydraulic fluids, or corrosion problems. Discovery of this type of contaminate requires a modification of program goals or a redesign of parts for the system.

2.2 Function-generated Contaminates: wear or system operational derivatives of the systems' structural or fluid materials.

These contaminates consist of two subcategories: wear generated by moving parts; and polymer films produced by heat and pressure stresses on hydraulic or lubrication oils. This type of contaminate can always be found in systems with moving parts. They can be evaluated to generate system reliability data or to identify weaknesses in the system[3].

1 Marmo, F. F. and J. Pressman, Definition Research Study, N73-30843, Final Report, Contract #NASW-2395, G.C.A. Corp. (1973)

2 Fogdall, L. B., Cannaday, S. S., Wilkinson, M. C., Crutcher, E. R., and Wei, P.S.P., Combined Environmental Effects on Polymers, Eighth Space Simulation Symposium Proceedings (1976).

3 Scott, D., Ferrography - An Advanced Design Aid for the 80's, Wear, 34:251-260 (1975).

2.3 Facility-generated Contaminates: particulate not related to the structural materials in the systems, or to the production or assembly cycle of the system.

This type of contamination generally indicates a source not anticipated in the design of the production flow diagram. Often this involves the failure of an air scrubbing system, process baths being used in unexpected ways, or some similar problem that was not foreseen in the selection of the facilities to be used during the production and assembly of the system. Examples include leaks in air systems that introduce contaminated air, surface films on parts as a result of using cleaning solutions as "stripping" baths, and rooms being "converted" into clean rooms unsuccessfully.

2.4 Activity-generated Contaminates: particulate can be explained in terms of the production cycle of the system.

The activities that are associated with the manufacture, assembly, and inspection of a part, or system, generate contaminates. The identification of these particulates can often pinpoint the time and place of contamination. Examples include plastic particulate from a swaging mandrel found in hydraulic tubing, or tooling residue in machined parts. Poor clean room technique is included in this category. Contamination consisting of epithelial cells, clothing fiber, and human hair in an otherwise clean system indicates a breach of clean room discipline.

## 3.0 ANALYTICAL APPROACH

### 3.1 The Relationship Between an Assemblage and a Source

The particulate in a contamination sample can generally be categorized into a general type with little difficulty. The task of the analyst is then to identify the source. The source identified must have relevance within the framework of the industrial environment. The identification of a diatom from a pre-cambrian silt may be interesting, but the breakdown of a filter containing diatomaceous earth is more relevant. This is a fanciful example of source analysis carried too far, but it points out the importance of communication between the analyst and the program involved. The "sources" which must be identified are those over which we have some control. The more the analyst knows about the system's construction materials and environment the easier the analysis becomes. Potential (relevant) sources suggest assemblages and minimum criteria required to determine the sourc It is much more difficult to fully characterize assemblages and then look for relevan sources. As Figure 1 points out a source implies an assemblage; an assemblage suggests a source.

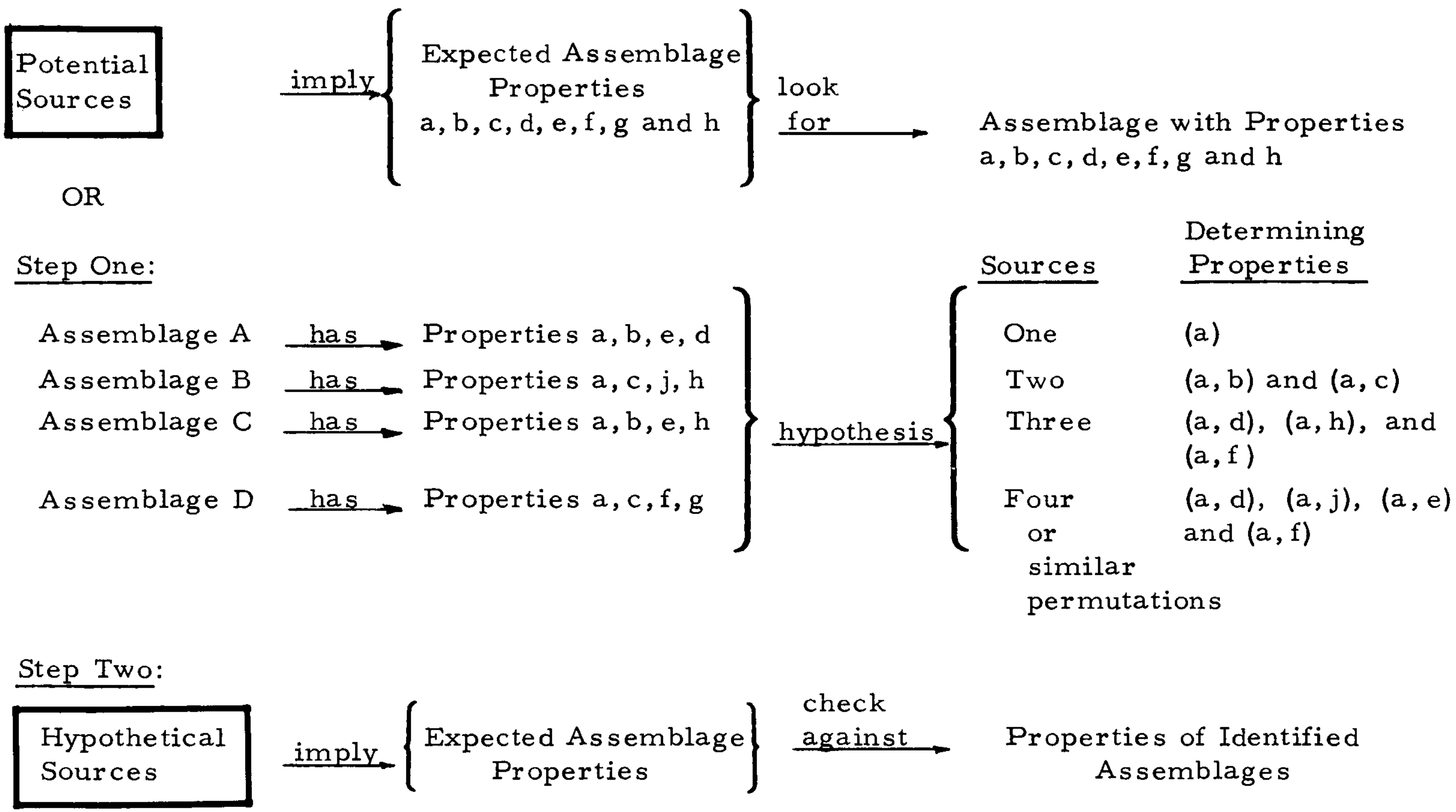


FIGURE 1: RELATIONSHIP BETWEEN ASSEMBLAGES AND SOURCES

### 3.2 Identification of Assemblages I: Analytical Approach

As with any other analytical scheme that is not of an in situ type, collection biases must be considered. Since the subject of this paper is not collection techniques, they have been presented only very briefly in Table #1. All are subject to some biases or limitations, the detailing of which would fill another paper.

Ideally, collection problems are minimal or the part is small enough to be brought to the laboratory for analysis. The first part of the analysis is a rapid overview of the part or collected sample using a low power stereoscopic microscope. Distribution gradients and gross size ranges involved are noted. The sample is then prepared for analysis on the analytical compound microscope. Microanalytical techniques are then used to identify the individual particles and to characterize the particulate distribution. Most of these techniques are described in the literature.[4,5,6]

The microscopic system used in this laboratory consists of a compound microscope using transmitted polarized light and oblique top light. Phase contrast is also used with polarized light and oblique top light to add to the optical data recoverable from a single mount. This microscopic system is the center of the total approach. Without microscopy assemblage analysis is not possible.

### 3.3 Identification of Assemblages II: Typical Assemblages

The individual particles found in the sample are characterized or identified and listed along with a brief indication of their quantity. This list suggests typical assemblages which are then tested by looking for other, as yet undetected members of these assemblages.

The following sections contain examples of contaminates that illustrate typical assemblages.

#### 3.3.1 Auto-generated Assemblages

For convenience auto-generated assemblages can be divided into three subdivisions based on the mechanics of their generation. Each has specific characteristics.

1. Outgassing Assemblages - Outgassing assemblages have two characteristic chemical properties:

4 Bowen, E. R. and Westcott, V. C., Wear Particle Atlas, N00156-74-C-1682, Final Report, Foxboro/Trans-Sonics, Inc. (1976).

5 McCrone, W. C. and Delly, J. G., The Particle Atlas, Ed. II, Ann Arbor Science, Ann Arbor, Michigan (1973).

6 Crutcher, E. R., The Role of Light Microscopy in Aerospace Analytical Laboratories, Ninth Space Simulation Symposium Proceedings (1977).

| METHOD | DESCRIPTION | COMMENTS |
| --- | --- | --- |
| 1. Liquid Flush of Surface | A clean liquid flows over the test surface and collects particulate. | Effective provided liquid much cleaner than surface and liquid can be collected for testing. |
| 2. Lift from Surface | Tape, collodion, cured rubber, treated filter, and similar materials can be used to lift particles from a surface. | Particulate is collected with its spatial distribution unchanged. Some methods form a cast of the surface area sampled. Some methods are limited as to the surfaces they may be used on. |
| 3. Filtration | Known volume of gas or fluid is drawn through a membrane filter, preferably a cellulose acetate. | If the filter is cellulose acetate a high quality permanent mount can be made. Other types of filters generally require more preparation before analysis. |
| 4. Other | Impaction, electrostatic precipitation, thermalphoresis, etc. | Techniques useful for collecting specific size ranges of particles. |

TABLE #1: SOME METHODS OF COLLECTING PARTICULATE

3.3.1 1. a. The outgassing product from a single source does not significantly vary from particle to particle; and

b. the individual particles are small, their size being determined by nucleation, flocculation, and coagulation type effects.

They also have a characteristic distribution with respect to the source consisting of:

a. A concentration gradient with distance; and

b. a shaped distribution controlled by media flow, diffusion effects, electrical forces, surface properties, and other similar effects.

2. Corrosion Assemblages -

Corrosion assemblages can be complex, stable, metastable, and unstable compounds of the original structural materials and some other reactant and/or catalyst. The particulate tends to consist of aggregated crystallites if the corroding structural material is a metal. The crystallites often exhibit a variety of sizes, but a single morphological habit. The particles will often be stratified or banded and porous. Polyorganic materials may become crystalline, similar to the metals, or simply alter into a particulate of mulitple organic phases. The filler material is often useful in the corrosion of a polyorganic material as a tracer. Most inorganic fillers are not effected by the chemical alteration of the organic and can be identified by their optical crystallographic properties.

3. Other Auto-generated Assemblages -

FEP teflon particles and aerosols of associated materials from dielectric breakdown in some orbital environments are an example of this type of assemblage. These assemblages are generally produced by some force other than friction acting on the structural material. Vibration, radiation, electric charge, and heat or cold ar common causes of this type of particulate assemblage.

### 3.3.2 Function-generated Assemblages

Function-generated, or wear assemblages, are usually very easy to identi or characterize. In most systems they consist of metal, gasket or seal material, and polymerized lubricant films. As a result of recent advance in diagnostic wear analysis there is a wealth of literature on typical, meta wear assemblages.[3,4] Wear polymers are not so well documented but most are easily identified by their characteristic structures.[7,8]

The motion of one surface against another produces a large number of submicrometer particles. Larger particles are also produced which can be used to diagnose more significant wear mechanisms. Break-in wear produces large numbers of elongated tablet shaped particles. Some cutting wear is usually generated as production abrasive-finishing particles work their way out of the metal during operational stress. The number of large wear particulate decreases after the break-in period and then begins to increase again as the system ages. The size, width/length ratio, length/thickness ratio, and diameter/thickness ratio are all related to the specific wear mechanisms active in the system. If the identification of the wear mechanism is not sufficient to identify the wearing part, individual particles can be selected for microprobe analysis. A comparison with the alloys in the system and the elemental analysis of specific particles will identify the alloy wearing and the wear mode. Similarly, the shape and quantity of friction polymers and gasket or sealant wear particulate can indicate the effectiveness of a given lubricant or the suitability of a gasket material or gasket configuration.

1. Wear Metal Assemblages

There are many types of characteristic assemblages. Most of these have a "typical" single morphology as a marker.

Bearing wear is marked by spherical metal particles 1-3 μm in diameter. These are produced in relatively small numbers compared to the exfoliated small flat tablets also produced by this type of wear. Spheres are only produced by bearing wear.[9]

7 Reda, A. A., A Note on the Investigation of Friction Polymer Rolling Pin Formation, Wear, 32:115-116 (1975).

8 Bose, A. C., Klaus, E. E., and Tewksbury, E. J., Evaluation of Wear Products Produced by Some Chemical Reactions in Boundary Lubrication, ASLE Transactions, 19; 4:287-292 (1975).

9 Loy, B. and McCallum, R., Mode of Formation of Spherical Particles in Rolling Contact Fatigue, Wear, 24:219-228 (1973).

Cutting wear produces long, thin particles. These particles are often similar to those produced by a lathe. Their cross section is often an indication of the size of the piston or cylinder anomaly that is causing the problem.[10]

Gear wear is marked by long, thick particles characteristic of the shear-roll action between teeth in a system of gears.

Other typical metal wear assemblages are detailed in Bowen and Westcott (1976).[4]

2. Gasket and Seal Wear Assemblages

Gaskets and seals normally consist of a plastic or elastomer with a filler. The discovery of these materials in the system is indicative of their wear. Normally free filler, plastic or elastomer and filler, and just plastic or elastomer will be found as a result of gasket or seal wear. Tapered cylinders of these materials are the most typical wear morphology.

3. Friction Polymers

Ideally, metal never touches metal in a properly lubricated system. The metal is shielded by a thin film of lubricating material. This material is often a solid or very viscose liquid between the metal parts. During operation this material is worn away, resulting in the generation of particulate referred to as friction polymers. There are three main morphologies in this material. "Rolling pins" is a term used to describe tapered cylinders of the lubricating film.[7] The cylinders are produced by a shearing action that rolls small sections of the film into cylinders. Thin flat films are another common shape friction polymer. These often contain spherulitic soap crystals. The last common structure is the result of a buildup of the friction film into relatively thick layers which then break free and float in the system.

As a final note on function generated assemblages, abrasive particles are common during the early operation of new machines. Production techniques involving the use of abrasives invariably result in some of the abrasive becoming embedded in the metal. With the expansion and contraction of operational stress these particles are released into th

10 Dean, S. K. and Doyle, E. D., Significance of Grit Morphology in Fine Abrasion, Wear, 35:123-129 (1975).

system. If an analysis of the systems contaminates indicates abrasives as the only non-wear particulate present in any significant amount the abrasives should be considered part of the function generated particulate.

### 3.3.3 Facility-generated Assemblages

Facility-generated assemblages contain a very complex variety of particulate types. They include airborne particulate and aerosols from all kinds of sources, natural or industrial. They also include liquid suspensions of natural material, precipitates, or industrial material residues. These assemblages are so varied that no "typical" assemblage will be listed, instead Table #2 is offered as an example of common particulate types.

As with the assemblage types mentioned earlier, a facility-generated assemblage has properties of its own beyond the elemental composition of its members.

Size Distribution: As a rule of thumb, the smaller the size distribution, the further removed from the source. Air conditioning systems, even if inefficient, tend to deliver particulate under 10 µm. Materials brought in on clothing or through doors often exceeds that size.

Shape:

High Spherulite Content: Spherulites are small spheres of crystalline material. Their two most common sources are air agitated process solution with high soluble salt content, or flux condensation from welding or similar operation involving a temporary fluid state. A high concentration of these types of particulate can often aid in the discovery of the source.

Spheres in general indicate industrial or human activity and are useful in indicating possible sources.

Spatial Distribution: As with outgassing, a characteristic distribution of the particulate is often helpful in identifying the direction of the source. In this case the source can generally be considered to be at infinite distance with contamination density a function of surface curvative with respect to the source. In process solution contamination two types of distributions typically occur. The first is a film of very fine particulate which may be nucleated or precipitated by the surface of the part in the solution, be collected by the part as it passes through the surface of the solution, or be the product of air exposure to a liquid phase contaminate film. These mechanisms often result in the contaminate being found on only the upper or lower surface of a part. The second type is characterized by randomly distributed contaminates caused by discrete single liquid or solid suspensions in the process bath.

| SOURCES | BIOLOGICAL PARTICULATES | INDICATION |
|---|---|---|
| Flowering Plants | Pollen, Plant Parts | Exposure to external environment, season |
| Molds, Fungus | Spores, Mycelium | Moist environment |
| Water Life | Diatoms, Algae | Unfiltered water, stagnant water |
| Animal and Insect | Insect Parts, Animal Hair | Insect or animal access open |
| **SOURCES** | **FIBER PARTICULATES** | **INDICATION** |
| Cloth | Synthetic & Natural, Colored, Colorless | Clothing, rags, rugs, etc. being used |
| Filters | Synthetic, Natural, Glass, Mineral | Startup or breakdown of filter |
| Insulation | Glass, Mineral | Exposed insulation |
| Reinforcing | Glass, Mineral, Graphite | Material failure |
| **SOURCES** | **INDUSTRIAL RESIDUE PARTICULATES** | **INDICATION** |
| Metal Forming | Tooling Particles, Weld Fume, Grinding Particles, Slags, Scale, Abrasives, Fluxes, etc. | Better cleaning required |
| Process Chemicals | Salt Spherulites, Reaction Residues, etc. | Better rinsing required |
| Construction | Cement Dust, Spray Paint, Plastics, Resins, etc. | Improved isolation required |
| Transportation | Wear Rubber, Asphalt, Flyash, etc. | More protection during transportation required |

TABLE #2: TYPICAL FACILITY GENERATED PARTICULATE

### 3.3.4 Activity-generated Assemblages

Every activity in the production of a system, from forming to assembly, produces particulate. Metal working activities, tooling, grinding, cutting, welding, etc., produce particulate similar to operational metal wear. It can generally be distinguished by its larger size and tendency to be more highly oxidized at the surface. Process solutions and heat treating operations may leave residues behind. Inspection of a part may result in contamination with human hair, clothing fibers, and dried, exfoliated skin.

These assemblages are often cataloged for a given program since they do not change once a production sequence has been determined. A given welding operation produces the same type of contamination regardless of the part it's applied to. Once such an operation is cataloged it serves as a reference for most future applications.

## 3.4 Identification of the Source:

Particulate contamination from a single source is the result of a complex set of variables which determine the types of particulate possible. As Figure #1 suggested, the identification of a source is a decision made on the basis of reasonable probability. The more unique the properties of a source's particulate assemblage the more certainly that source can be quickly and easily identified. The fact that a completed system invariably contains more than one assemblage from multiple sources complicates the task of identifying the major source of contamination. Figure #2 demonstrates the relationship between one type of particulate, its assemblage, and its source. The best method of determining the source of contamination is to test the suspected source and compare the contamination assemblages with the assemblage from that source. Experience and a well stocked reference slide cabinet will increase the speed and the specificity of this type of analysis.

# 4.0 CONCLUSIONS

The identification of contamination sources using assemblage analysis has very definite economic advantages. No other analytical approach is capable of evaluating typically small, heterogeneous samples as completely or as quickly. Assemblage analysis is not a single instrument approach. Although an analytical microscope is essential many other instruments can be used to aid in the identification of specific substances. This technique offers an approach which synergistically combines different analytical capabilities to solve problems.

| PARTICULATE | ASSEMBLAGE | SOURCE |
|---|---|---|
| Emery | Breakin wear metal<br>Silicon carbide<br>Emery dominant mineral species | Breakin Wear |
| | Silicon carbide<br>Emery dominant mineral species<br>Resin binder material may be present<br>Metal and metal oxide spheres<br>Large cutting type metal particles<br>Fibers, Iron oxide | Production Activity Generated |
| | Silicon carbide<br>Emery<br>Quartz<br>Feldspars<br>Industrial residues<br>Fibers<br>Biologicals, Soot, Iron oxide, etc. | Exposure to General Industrial Environment |
| | Quartz<br>Feldspars<br>Pyroxenes<br>Emery<br>etc. | Natural Mineral Assemblage |

FIGURE 2: THE RELATIONSHIP BETWEEN A CONTAMINANT, ITS SOURCE AND ITS ASSEMBLAGE

The economic benefits that can be derived from this approach begin in the early design phase of a program and follow the program through to routine production. In the early prototype, or materials testing portion of a program, assemblage analysis techniques can be used to detect contamination autogenerating mechanisms. Early detection of these mechanisms can cut weeks off a testing program that is doomed to failure and identify the problem before it damages effective parts of a prototype. Wear problems are also identified at a stage of development long before a failure occurs in the part. Both wear mechanisms and wearing surface are identified thus supplying specific direction to design modifications.

In the event of a system failure assemblage analysis can often identify the root cause. Material selection problems give rise to autogenerating mechanisms, design problems result in excessive wear, production quality control problems produce facility-generated contaminates, and production plan problems produce activity-generated contaminates.

These same techniques can be used to help solve problems that arise during a products working life. Different operational environments, a change in subcontractor, or a modification of the production sequence can give rise to unexpected, though often easily solved problems.

The economic benefits that can be derived as a result of this analytical approach are significant. This technique differs from most current approachs in that conclusions are based on the total sample rather than one compound or a collection of elemental data. This technique has produced very significant cost and product reliability benefits for us. Its future application will undoubtedly increase those benefits.

## 5.0 REFERENCES


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